RESEARCH ARTICLE

Naphthalene Based Fluorescent Probe for the Detection of Aluminum Ion

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ABSTRACT: This work reports on the naphthalene based chemosensor for selective detection of Al^{3+} in aqueous solution based on photoinduced electron transfer (PET) process. Fluorescent sensors with naphthalene unit have been prepared and characterized. Their complexation behavior and binding mode towards Al^{3+} and other metal ions have been studied by UV-vis, fluorescence spectrometric and Mass Spectrometry method. Receptor 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol, exhibits highly selective and sensitive recognition of Al^{3+} over other heavy and transition metal ions. The "off-on" fluorescent recognition of Al^{3+} by 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol is free from the interference of other metal ions. Therefore, the sensor 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol could be used as a potential probe to detect aluminum ions in the biological and environmental monitoring works.

KEYWORDS: Naphthalene, Fluorescent Probe, NMR, FT-IR, Aluminum, sensor, Mass Spectrum

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1. INTRODUCTION

The development of sensors for the detection of cations, anions and neutral species in solution has always been of great interests in environmental and biological systems. Several methods, such as high-performance liquid chromatography, mass spectrometry, atomic absorption spectroscopy, inductively coupled plasma atomic emission spectrometry, electrochemical sensing, etc., have been developed to analyze the targets concerned [1-6]. However, these methods suffer from extensive and time-consuming procedures that involve the use of sophisticated instrumentation. The fluorogenic method has been a powerful tool due to its simplicity, inexpensive, rapid implementation, and high detection limit with bioimaging applications [7].

Fluorescent probes enable researchers to detect particular components of complex biomolecular assemblies, including live cells, with exquisite sensitivity and selectivity. Fluorescent chemosensors have been developed to be a useful tool to sense in vitro and in vivo biologically important species such as metal ions and anions because of the simplicity and high sensitivity of fluorescence assays. A typical fluorescent chemosensor contains a receptor (the recognition site) linked to a fluorophore (the signal source) which translates the recognition event into the fluorescence signal [8,9]. Therefore, an ideal fluorescent chemosensor must meet two basic requirements: firstly, the receptor must have the strongest affinity with the relevant target (binding-selectivity). Secondly, on the basis of good binding-selectivity, the Fluorescence signal should avoid environmental interference (signal-selectivity), such as photobleaching, sensor molecule concentration, the environment around the sensor molecule (pH, polarity, temperature, and so forth), and stability under illumination. According to the well-known fluorophore–spacer–receptor scaffold, the receptor is the central processing unit (CPU) of a chemosensor [10-12]. Although the ultimate aim for a fluorescent chemosensor is to image the target of interest in a biological setting, a thorough understanding of the available constructs can help to elucidate and improve the design of chemosensors.

Compounds of Aluminium widely present in the environment in various ways, namely from water treatment plants, food additives medicines, antiperspirants, deodorants, Aluminium cookware, bleached flour, anti-acids, production of light alloys etc. Excess of Al^{3+} has been inducing Parkinson's disease, amyotrophic lateral sclerosis and so forth. Although Al^{3+} is widely used in our day to life, it is a non-essential element for living systems. According to the world health organization (WHO) report the average daily intake of aluminum in humans is around 3-10mg. WHO as listed Al^{3+} as a source of food pollution and limited its drinking water concentration 7 to 41mM. Therefore, the development of chemosensor for the rapid detection of Al^{3+} is highly desirable [13,14].

The naphthalene moiety is one of the most effective fluorophores for the design of fluorescent chemosensors. Herein, we designed and synthesized a highly selective fluorescent chemosensor for Al^{3+} based on naphthalene derivative. Studies on the synthesis of the final receptor and its response towards the aluminium ion based on

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photoinduced electron transfer (PET) process will be completely focused on this present work.

In this paper, we report a new type of naphthalene-fluorescent chemosensor for the aluminum ion based receptor, which contains an imidazole unit having two nitrogen atoms and one hydroxy group on naphthalene moiety as the binding sites. Fluorescent sensors with naphthalene unit have been prepared and characterized. Their complexation behavior and binding mode towards Al^{3+} and other metal ions have been studied by UV - vis, fluorescence spectrometric and Mass Spectrometry method. However, before going into our works the following gives a brief account of the Aluminium sensors reported in the literature so far.

EXPERIMENTAL METHODS

2.1. Materials and instruments

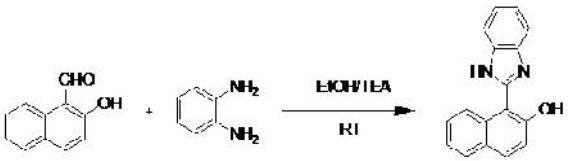
All solvents were purchased commercially with reagents grade quality. O-phenylenediamine was obtained from Merck and was used without further purification. ^1H NMR and ^{13}C NMR spectra were recorded on a Brucker 400 MHz spectrometer, DMSO solution with TMS as an internal standard. LC-MS were determined on an LC-MSD-Trap-XCT Plus based on infusion methods. Absorption spectra were made on a Shimadzu UV-240 spectrophotometer. Fluorescence measurements were performed on a Jasco FP-8200 spectrofluorimeter equipped with quartz curettes of 4 cm path length. The excitation and emission slit widths were 5.0 nm. All absorption and emission spectra were recorded at 24 ±1 ^{0}C. Stock solutions for analysis were prepared (2 x 10^{-3}M for compound **1** (CH_3CN/H_2O, 1:1 (v/v), HEPES=50 mM, pH=7.0) immediately before the experiments. The solutions of metal ions were prepared from chloride and nitrate salts of Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Cd^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cr^{3+}, Zn^{2+}, Pb^{2+}, Hg^{2+}, Al^{3+}, Fe^{3+}, La^{2+},Fe^{2+} and Ag^+.

2.2. SYNTHESIS

2.2.1. Synthesis of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol (1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol)

Appropriate o-hydroxy naphthaldehyde (0.2 g, 1.162 mmol) was dissolved with ethanol (20mL) in the presence of triethylamine and o-phenylenediamine (0.15 g, 1.39 mmol) stirred for 5 h in room temperature. The reaction mixture was cooled, and the precipitate was filtered and recrystallized from DMF to give the above-mentioned compound **1.**

Red colour Solid (80% yield). Mp: 232^{o}C; FT-IR (KBr), cm^{-1}: 1384, 1543, 1608, 2360, 3400. ^1H NMR (300 MHz, $CDCl_3$): 9.45 (s, 1H), 8.11-8.19 (q, 1H), 7.71-7.86 (m, 2H), 7.10-7.57 (m, 5H), 6.81-6.88 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): 109.15, 114.81, 115.74, 118.81, 119.46, 120.19, 123.16, 126.84, 127.18, 127.72, 127.94, 128.86, 135.29, 141.55, 155.67, 166.47.



Scheme 1: Synthesis of receptor 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol

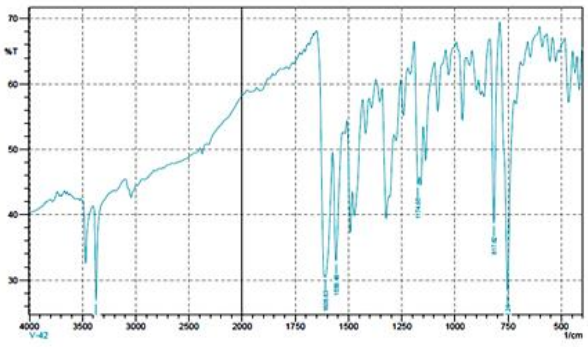


Fig. 1: FT-IR spectrum of 1- (1H-benzo [d] imidazol-2-yl) naphthalene-2-ol

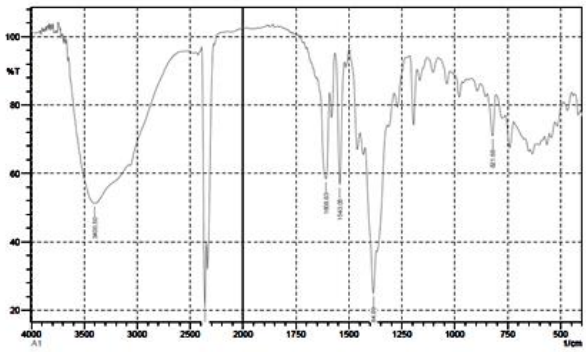


Fig. 2: FT-IR spectrum of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol + Al $(NO_3)_3$

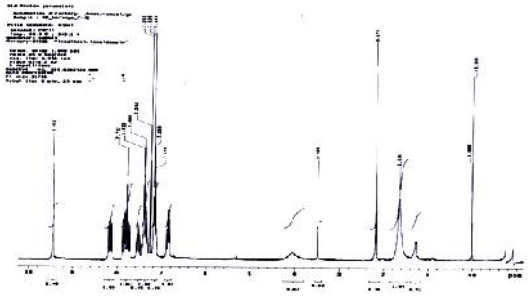


Fig. 3: ^1H NMR spectrum of 1-(1H-benzo [d] imidazol-2-yl) naphthalene-2-ol

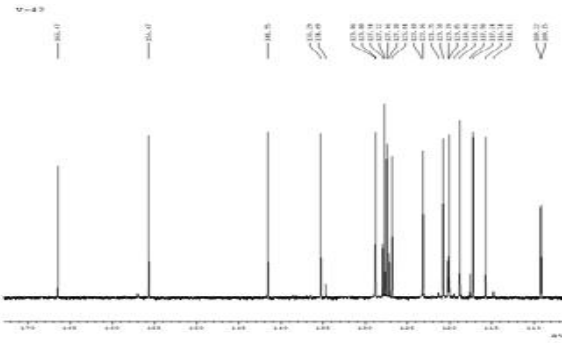


Fig. 4: ^{13}C NMR spectrum of 1-(1H-benzo [d]imidazol-2-yl) naphthalene-2-ol

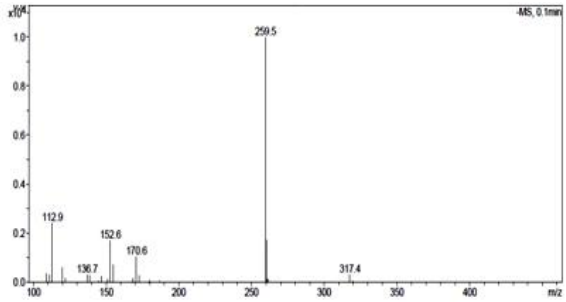


Fig. 5: Mass spectrum of 1-(1H- benzo[d] imidazol-2-yl) naphthalene-2-ol

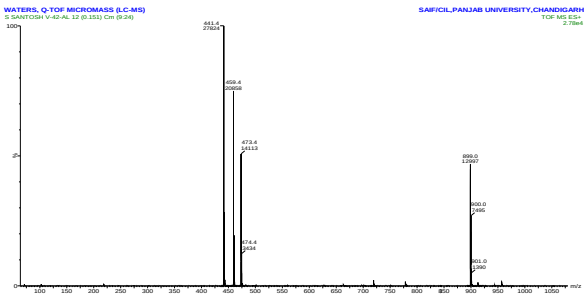


Fig. 6: Mass spectrum of 1-(1H-benzo [d] imidazol-2-yl) naphthalene-2-ol +Al $(NO_3)_3$

RESULTS AND DISCUSSION

3.1. Synthesis and characterization of receptor 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol

Herein, naphthalene was chosen as the fluorophore, by virtue of its excellent photophysical properties, such as good photostability and strong absorption and emission signals. The fluorescent receptor 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol was concisely synthesized from 2-hydroxy naphthaldehyde and o-phenylenediamine in single step Schiff base followed by cyclization reaction (Scheme 1). The final receptor 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-*ol was* verified by NMR (^1H and ^{13}C) and mass spectrometry.

3.2. The selectivity of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol towards Al^{3+}

Screening of the metal ion binding ability of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-*ol was* carried out in CH_3CN-H2O (1:1 v/v, HEPES 50 mM, pH=7.0) solution. Receptor 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-*ol was* non-fluorescent, upon addition of 100 equiv. of Al^{3+} to a solution of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol significant enhancement of fluorescence with an emission maximum at 506nm was observed. However, the same concentration of other metal ions (Na^+, K^+, Pb^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, La^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Mn^{2+}, Cr^{3+}, Ba^{2+}, Ce^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+} and Ag^+) produced only minor changes in the fluorescence spectra (Fig. 7). Therefore, 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol was a highly selective fluorescence ''off-on'' probe for Al^{3+} in CH3CN-H_2O (1:1 v/v, HEPES 50 mM, pH=7.0) solution [15].

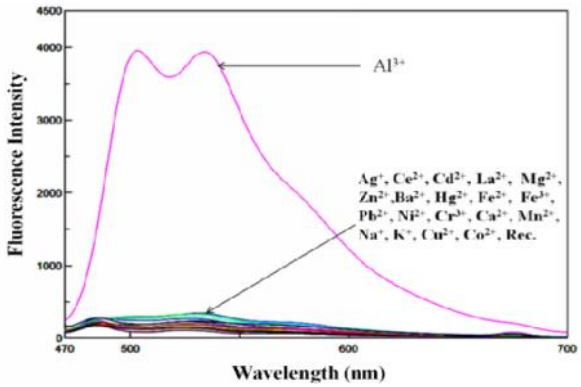


Fig. 7: Fluorescence spectral changes of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol (4 x 10^{-6} M) CH_3CN-H_2O solution (1:1 v/v, HEPES 50 mM, pH=7.0) in the presence of various metal ions (100 equiv. of each, excited at 450 nm)

The possible interferences by other metal ions were carried out through competitive complexation experiments. The fluorescence changes of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol were measured by the treatment of 100 equiv. Al^{3+} ions in the presence of the same equiv. other interfering metal ions including Na^+, K^+, Pb^{2+}, Cu^{2+}, Cd^{2+}, Hg^{2+}, La^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Ca^{2+}, Mn^{2+}, Cr^{3+}, Ba^{2+}, Ce^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+} and Ag^+. The tested interfering metal ions showed no obvious interference with the detection of Al^{3+} ion (Fig.7). These results suggested that receptor 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol could be used for the selective detection of Al^{3+}-ion in real sample analysis [14].

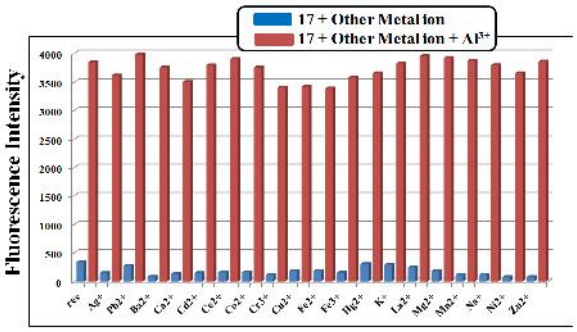


Fig.8: Competition analysis of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol (4×10^{-6} M) in CH_3CN/H_2O (1:1 v/v, HEPES = 50 mM, pH = 7.0) solution. The blue bars represent the fluorescence emission of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol and 100 equiv. of other metal ions. The red bars represent the fluorescence changes that occur upon addition of 100 equiv. of other metal ions to the solution containing 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol and Al^{3+} (100 equiv.)

3.3. Binding studies of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol with Al^{3+}

The fluorescence titrations of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol were carried out by the gradual addition of various amounts of Al^{3+}, respectively. As shown in Fig.7, an increase of fluorescence intensity could be observed with increasing Al^{3+} concentration (0-100 equiv.). The fluorescence change almost saturated upon addition of 100 equiv. of Al^{3+}, implying that 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol interacts with Al^{3+} in 1:1 stoichiometry [15].

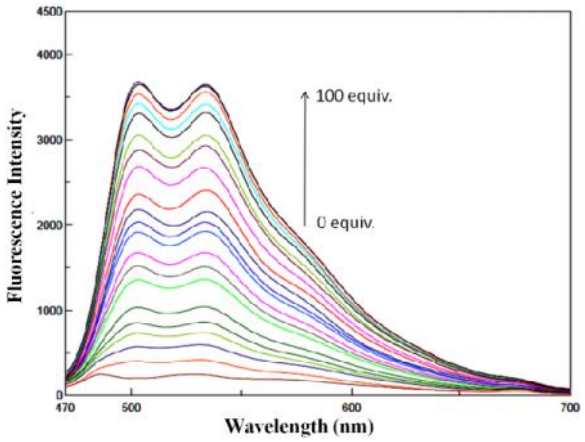


Fig. 9: Fluorescence titration spectrum of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol (4 x 10^{-6} M) in CH_3CN-H_2O solution (1:1 v/v, HEPES 50 mM, pH=7.0) upon addition of different amount of Al^{3+} (0-100 equ. of each, excited at 450 nm) emission = 506 nm

3.4. Job's plot and association constant analysis

Binding analysis using the Job's plot method reported in Fig. 10, helps to find out the complexation mode in the 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol – Al^{3+} (Host-Guest) complex. The complex showed a maximum mole fraction of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol is 0.5 at 506 nm established a 1:1 (1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol : Al^{3+}) binding stoichiometry.

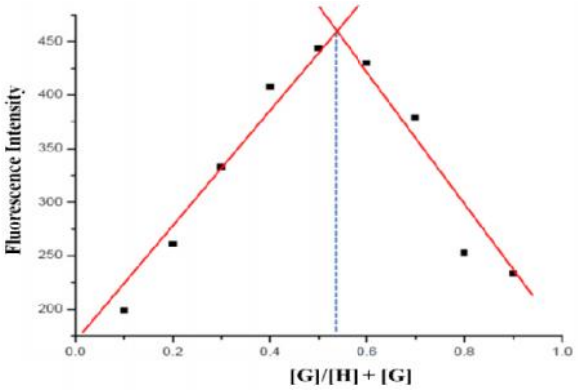


Fig. 10. Job plot of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol and Al^{3+} ([1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol] + [Al^{3+}] = 1 µM) in CH_3CN-H_2O solution (1:1 v/v, HEPES 50 mM, pH=7.0).

The binding stoichiometry between 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol – Al^{3+} was also confirmed by the Benesi–Hidebrand nonlinear curve fitting method Fig.11. The association constants were determined to be Ka = 2.783 x 10^3 M^{-2} for the 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol – Al^{3+} complex.

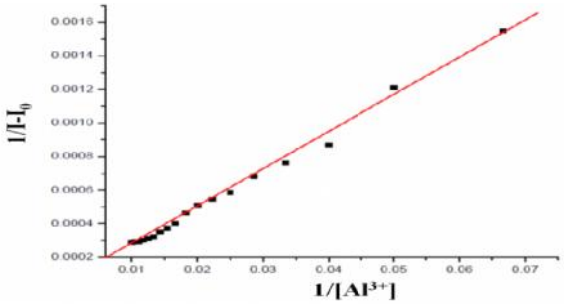
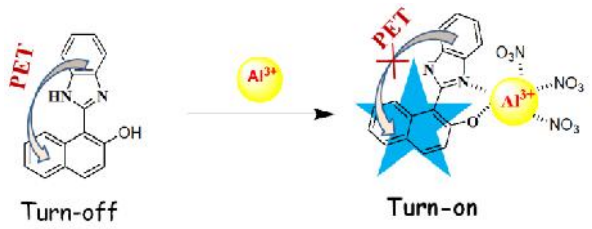


Fig. 11. Benesi–Hildebrand plot (emission 506 nm) of 1- (1H-benzo[d]imidazol-2-yl) naphthalene-2-ol - Al^{3+} complex (1:1) binding stoichiometry.

3.5. Proposed binding mode of the complex

The binding mechanism was investigated through fluorescence changes as shown in scheme 2. For the sensor 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol, have weak fluorescence due to intramolecular photo-induced-electron-transfer (PET) process within the naphthalene unit. Upon addition Al^{3+}-ions in 1-(1H-

benzo[d]imidazol-2-yl) naphthalene-2-ol, created good fluorescence enhancements and totally block the PET process. Based on the fluorescence titration spectrum, job's plot and non linear curve fitting (Benesi-Hildebrand) methods were reveals that 1:1 binding ratio between 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol - Al^{3+} complex. From these data, it could be deduced that the possible coordination modes of 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol - Al^{3+}- ion complex was 1:1 (Host: Guest) binding stoichiometry [16,17].



Scheme 2. Proposed binding mode of 1-(1H-benzo [d] imidazol -2-yl) naphthalene-2-ol with Al^{3+}

CONCLUSION

We have reported a new naphthalene benzimidazole conjugate 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol as a sensor for Al^{3+} ions in CH_3CN-H_2O solution (1:1 v/v, HEPES 50 mM, pH=7.0). Receptor 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol**,** exhibits highly selective and sensitive recognition of Al^{3+} over other heavy and transition metal ions. The "off-on" fluorescent recognition of Al^{3+} by 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol, is free from the interference of other metal ions. Hence, the sensor 1-(1H-benzo[d]imidazol-2-yl) naphthalene-2-ol, could be used as a potential probe to detect aluminium ions in the biological and environmental monitoring works. Further studies on the bioimaging application are underway. In addition, derivatives of the naphthalene benzimidazole conjugates by changing the fluorophore, ionophore and the spacer are also in progress for effective metal ion sensors.

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